

Spectroscopic Studies of Conjugated Polymers for use in Organic Solar Cells

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Abstract

Spectroscopic Studies of Conjugated Polymers for use in Organic Solar Cells. Aimee Ginley (Massachusetts Institute of Technology, Cambridge, Massachusetts 02139) Garry Rumbles (National Renewable Energy Laboratory, Golden, Colorado 80401).

Organic based solar cells (polymer and small molecule) have the potential to be cheaper and more environmentally friendly to produce than conventional semiconductor cells. However, because of their different opto-electronic properties, organic solar cell will need to have very different configurations than traditional solar cells. Various processing approaches are currently being evaluated to determine if they can produce optimized organic solar cells. It is critical to develop an understanding of how process methodology effects the behavior of the organic materials. In this work, different methods of drying polymer thin films were investigated to better understand the critical step of solvent removal in thin film production. Tests were also done to determine whether the addition of a dopant increased the mobility of the conjugated polymers. The experiments investigating different thin film drying methods showed that heating the polymer while drying led to lower fluorescence. The lower fluorescence could be due to the desired goal of higher hole mobility. The doping tests resulted in lowered polymer absorbance and relatively constant fluorescence for oxidized MEH-PPV. The constant fluorescence could be due to the excitons and polarons not interacting in the doped polymer. It could also be due to the excitons and polarons not interacting. This is an unexpected result which will be investigated further.

Category: _____

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Introduction

Today there is a general agreement that fossil fuels will not sustain the world's current energy uses forever. It is also known that the use of fossil fuels can have negative environmental effects such as acid rain and global warming. These problems can, in part, be alleviated by the use of alternative energy sources. This is especially true for renewable energy resources such as solar power, wind and biomass. One approach is the use of solar cells to convert sunlight to electricity. Silicon based solar cells (crystalline or amorphous) are the current choice for commercial uses. However, the current cost of energy from solar cells, including installation, is generally at least an order of magnitude higher than that from more traditional energy sources. The production of Silicon based solar cells also generates CO₂ and other pollutants (Shah, 1998). For these reasons, scientists are looking for alternatives to silicon based solar cell. One of these alternatives is organic based solar cells, which use molecular or polymeric carbon based compounds in place of silicon.

The organic/polymer solar cells have the potential not only to be as efficient as silicon solar cells, but to be cheaper and cleaner to produce. Our group is focusing on polymer based organic solar cells. This type of solar cell is made up of a substrate (often glass) coated with a layer of a transparent conducting oxide (TCO), to act as a transparent contact. On top of the contact is a high surface area layer of an oxide (TiO₂ or ZnO). Coated on the oxide is a thin layer of a conjugated polymer (M3EH-PPV for example) and there is a final metallic top contact. A conjugated polymer is a long molecule consisting of repeating monomer units which have alternating double bonds along the carbon backbone. The extended pi delocalized in the electron orbitals creates an overlap of the electrons, which enables the polymers to carry current and absorb visible light and thus act as a semiconductor.

The solar cell functions when light comes in through the substrate and is absorbed by the conjugated polymer. This excites an electron to an excited state generating an electron/hole pair, however unlike the semiconductor the electron and the hole (the empty electronic state from which the electron came) stay bound to each other and travel together. This bound entity is called an exciton. Excitons can be destroyed by a number of mechanisms including separation into a separated electron hole pair (desired), radiative decay to the ground state by emitting light and non-radiative decay to the ground state by generating heat. When an exciton reaches the polymer/oxide interface the exciton splits. Typically conjugated polymers are effective hole transporters but do not transport electrons well, so when the exciton is split, the hole stays in the polymer and the electron is injected into the oxide. This path is energetically favored as well. Work is performed by the solar cell when the electron and hole are recombined at the far side of the device after passing through the circuit. To create an efficient solar cell excitons and holes must be transported effectively and the split exciton must not recombine at the polymer/oxide interface.

One of the drawbacks of polymer solar cells is the polymer's low hole and exciton mobility. The low mobility means that only a very thin section of the polymer close to the disassociation interface can be used for charge production. To try and increase the mobility, dopants are added to the polymer. To increase the hole mobility for example the polymer can be oxidized with NOSbF_6 so as to add an artificially large number of holes. This should work in theory, however it is unclear whether the oxidant is oxidizing the polymer in a productive manner, or if it is ineffective due to oxidation of impurities or other unknown reasons. To better understand this tests were done adding NOSbF_6 of known strength to MEH-PPV in

chlorobenzene solution. Learning how to control the doping of polymers and thus control the transport of holes, excitons and electrons is a key area of research in this field.

In the case reported here we use a strong oxidant, NOSbF_6 , to try and make the MEH-PPV polymer a better hole carrier. The MEH-PPV polymer we are using have the property that after they absorb light the excitons can decay emitting a characteristic wavelength of light, this property is fluorescence. The fluorescence of the polymer is being used to monitor the effects of the NOSbF_6 oxidant on the polymer.

For organic solar cells to be cost effective and to employ optimum process methodologies, the different production variables for generating the solar cells must be tested and understood. One of variables that is under study is the method for drying the polymer into a thin film. The goal is to be able to produce optimum thin films in a way that uses a minimal amount of potentially toxic chemicals and expensive, hard to operate equipment and minimizes energy use. For this reason we evaluated how the cheaper easier method of heat drying with a roughing vacuum compares to drying under high vacuum (10^{-6}).

Materials and Methods

For the first experiment performed, the different drying methods for polymer thin films were compared. To make the thin films MEH-PPV polymer was dissolved in chlorobenzene (Figure 1). The alternating single and double bonds along the backbone of MEH-PPV carry the charge, and the “arms” hanging off the benzene backbone make MEH-PPV soluble in a number of solvents. The polymer solution was then spun down on glass substrates (cut glass microscope slides) with a spin coater at approximately 2,000 rpm. A total of four thin films were made. Of

these films two were heated to approximately 100 C under roughing vacuum and two were dried in vacuum under 10^{-6} mtorr. After drying, absorbance measurements were taken on the films from 400 to 800 nm (Figure 3).

Fluorescence measurements were also taken with a Fluorolog (Figure 2). Two different experiments were done with the Fluorolog, an emission and an excitation test. Both experiments were performed with 1.5 mm slits on the monochromator, and a 400 nm band pass filter to allow only light with wavelengths higher than 400nm to hit the sample. Because the samples were thin films, the fluorolog had to be set on a front face geometry. This means that the emitted light from the fluorescing sample is detected at a 22.5 degree angle from the excitation light and some of the excitation light is picked up by the detector. For the emissions test, the emission detector was set to scan from 400nm to 800nm. Each sample was scanned with excitation wavelengths of 450nm, 500nm and 550nm. The excitation tests were performed by detecting at a constant emission wavelength while changing the excitation light wavelength. The excitation light was set to scan from 400nm to 700nm. For each sample the detector was set at 590nm, 634nm, and 700nm. These were the wavelengths at which peaks were seen during the emissions test. At the end of the experiment each sample had a data set consisting of one absorbance spectrum, three emissions test, and three excitation tests.

To further test the heat versus high vacuum drying techniques for polymer thin films, a second experiment was performed on the films that had been dried under high vacuum. One of the samples was heated to approximately 100 C under a roughing vacuum. The other sample was not changed so that it could be used as a control. The same experiments that were originally performed on all four samples were redone on the newly heated sample and the control.

To perform the experiments to evaluate the efficiency of doping the polymer by oxidation, the strength of the oxidant NOSbF_6 needed to be determined. Oxidation of a solution of **Zinc Tetraphenyl Porphyrin** (ZnTPP) in toluene was employed to do this. We investigated the conversion of ZnTPP to ZnTPP^+ . ZnTPP is a small organic molecule, not a polymer. It was used because it has a known extinction coefficient, and by applying the formula:

$$\text{Absorbance} = (\text{extinction coefficient})(\text{concentration})(\text{length})$$

we were able to calculate the concentration of ZnTPP before and after oxidation, and use this information to calculate how much of the oxidant added was actually oxidizing the ZnTPP.

To do the calibration, 2.5 mL of ZnTPP solution was added to a polished quartz cuvette. An absorbance spectrum was then taken on the sample from 350nm to 1000nm. A 0.95 mM solution of NOSbF_6 in CH_3CN was then added to the ZnTPP 50 μL at a time until a total volume of 350 μL of NOSbF_6 had been added. After each 50 μL addition of NOSbF_6 an absorbance spectra was taken.

The experiment was repeated three days later with the rest of the solution made for the first test. This experiment used the exact same conditions as the previous experiment; the only change was that the oxidant solution was older. This was done to see how stable the oxidant solution was.

After the initial calibration tests with ZnTPP, a solution of MEH-PPV was made up with 0.005g of MEH-PPV in 8mL of chlorobenzene. This solution was eventually diluted to 0.000312g of MEH-PPV in 20 ml of chlorobenzene in order to obtain reliable absorbance readings. A solution of 0.95 mM NOSbF_6 calibrated with ZnTPP was then added to the MEH-PPV in first 25 μL , then 50 μL , and finally 100 μL increments. Each of the NOSbF_6 /MEH-PPV solutions was had absorbance readings taken from 350nm to 1000nm. The different solutions

also had fluorescent measurements taken from 400nm to 850nm while being excited at 450nm and then at 500 nm. This data was then analyzed to determine the effect of the oxidant on MEH-PPV mobility.

Results

First we will report on the data from the MEH-PPV experiment testing the different drying methods of thin films. In the first part of the experiment with the four films, two heat dried and two vacuum dried, the fluorescence measurements were of the most interest. The fluorescence measurements showed that the MEH-PPV thin films that were dried under high vacuum fluoresced more than those that were dried under low vacuum at approximately 100 C (Figure 5). In the later experiment, the fluorescence of the MEH-PPV film that was dried under high vacuum and then subsequently heated at approximately 100 C went down in comparison to the control MEH-PPV thin film that was only dried under high vacuum (Figure 6).

The absorbance data for the four MEH-PPV thin films showed that those that were dried under a roughing vacuum and heated at approximately 100 C had a higher absorbance than those films that were dried under high vacuum only (Figure 7). However, the absorbencies were close enough that this difference may not be important.

In the second set of experiments the polymer was oxidized to various controlled extents while the optical properties were monitored. When the ZnTPP experiment was done to calibrate the amount of active NOSbF_6 in solution the absorption peak at 550nm was seen to decrease approximately half with the addition of 300 μl of oxidant. Multiple isosbestic points were present in the absorbance graph, these are single points through which all the absorbance lines pass,

indicating a fixed stoichiometry. There was also a small peak visible at the base of the higher wavelength side of the 550nm absorption peak (Figure 8). Another peak also grew in around 650nm as the oxidation increased. The absorbance data along with the extinction coefficient of $22,700\text{M}^{-1}\text{cm}^{-1}$ for ZnTPP was used to find the percentage of oxidant active in our solution (Harriman, 1989).

A at 550 nm 0 μl oxidant=	2.153	A=ECI	C=concentration
A at 550 nm 200 μl ox. =	1.645	C= 9.485×10^{-5} mol ZnTPP	
200 μl /0 μl =	1.645/2.153=.764 unoxidized		8%=dilution correction
1-0.764=	.236		
23.6%-8%=	15.6% oxidation with 200 μl oxidant		
9.485×10^{-5} mol x .156=	14.80 μM oxidized		
14.50 μM x $2.5 \times 10^{-3}\text{L}$ =	37nmol		$2 \times 10^{-4}\text{L}$ =oxidant added
37nmol/ $2 \times 10^{-4}\text{L}$ =	185 μM		Oxidant=.95mM
185 μM /950 μM =	19.5% active oxidant		

It was determined that 19.5% of the NOSbF_6 in the first experiment was active. Three days later 6.3% of the oxidant was active in the NOSbF_6 .

When the third ZnTPP calibration was done on a fresh ZnTPP solution before the oxidation tests with MEH-PPV, the oxidant solution was 13.39% active. It took much more oxidant to oxidize the MEH-PPV solution to see essentially the same absorbance change as the ZnTPP. 800 μl of oxidant were added to 3ml of MEH-PPV to approximately half the absorbance. There was also an isosbestic point present in the absorbance spectra, but no peak grew in with increasing oxidation (Figure 9), which was somewhat surprising.

The fluorescence spectra, unlike the absorbance data did not decrease significantly with increased oxidation, which was not expected. It also, as expected, had no isosbestic point. The spectra also showed a slight blue shift as the oxidation increased. Though this may be an

experimental artifact. This means that the edge of the spectra shifted towards the blue wavelengths of light with each successive oxidation step (Figure 10).

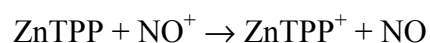
Discussion and Conclusions

For the experiment comparing the thin films that were dried by either being heated under roughing vacuum or under high vacuum, it was concluded that heating decreased the fluorescence. This decrease in fluorescence could be due to multiple reasons, and currently the specific cause cannot be determined. One hypothesis for the fluorescence decrease is increased mobility of excitons in the thin film. If the mobility of the excitons increased with heating, they would be able to travel further through the film. This would mean that a larger number of the excitons could travel to the glass slide and be quenched there. If more excitons are quenched it means there are fewer to emit light.

The decreased fluorescence could also be due to increased aggregation in the polymer chains. A region of aggregation is one where the polymers line up in an ordered manner. An example of this would be polymer chains lining up in a parallel manner for a short distance. It is hypothesized that these regions of aggregation trap excitation. This means more aggregation would trap a larger percentage of the excitation and prevent it from emitting as light.

Increased mobility is a positive property of polymers for solar cells. It may be beneficial to heat dry polymer thin films. In support of this hypothesis, solar cells that were made with heat dried thin films proved to be more efficient than those solar cells made with thin films dried under high vacuum.

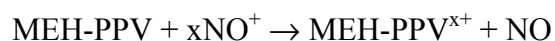
The first two tests with the calibration of NOSbF₆ using ZnTPP were useful in understanding the lifetime of the oxidant solution. The large decrease in active oxidant over a three day period alerted us to the fact that the NOSbF₆ solution decayed even when it was sealed in a bottle. Because of this the later tests were performed within as short a time period as possible between the initial ZnTPP calibration and the actual MEH-PPV oxidation experiment. The peak in the absorbance at 550nm decreased with added oxidant was representative of the decrease in the ZnTPP species in solution. The peak at 650nm that grew in as oxidant was added was representative of the ZnTPP⁺ species that was appearing in solution due to the reaction:



Unfortunately, the small peak observed to the side of the 550nm peak is hypothesized to be due to a corruption of the ZnTPP calibration data. This could be due to aggregation in the ZnTPP solution caused by overly high concentration or an impurity in the ZnTPP or solvent. Most likely this means that the ZnTPP calibration data is not completely accurate and new samples must be found or a new test must be designed.

The MEH-PPV oxidation experiment had results that were unexpected. To oxidize the MEH-PPV halfway (reduce the absorbance peak height by one half) required nearly three times the amount of oxidant that was required to oxidize the ZnTPP. This means that the polymer is much more resistant to oxidation than ZnTPP. However, this needs to be retested with calibrated concentrations of both MEH-PPV and ZnTPP.

Unlike ZnTPP, for which one molecule of ZnTPP is oxidized per molecule of active NOSbF₆, it is much harder to understand what is happening when MEH-PPV is oxidized. The reaction taking place for the oxidation of MEH-PPV is:



This means that different length polymers lead to different oxidation possibilities. Very short polymer chains could react completely differently than long polymer chains.

It was also interesting that there appears to be no new peaks growing into the MEH-PPV absorbance spectra with increased oxidation. This could mean a couple of things. First it could mean that no new species is appearing in solution. Second the new MEH-PPV⁺ species could have an absorbance peak in approximately the same position as that of the MEH-PPV. This would mean that the absorbance peak of the new MEH-PPV⁺ species could not be seen until more oxidant was added and the MEH-PPV absorption peak decreased sufficiently.

If real, the blue shift seen in the MEH-PPV spectra with the addition of oxidant could be due to a particle in a box effect. The positive charges added to the MEH-PPV backbone could essentially create a barrier that the excitons could not pass. This means that with each addition of oxidant, the area the excitons can move in becomes smaller. As per the particle in a box effect, the smaller the area in which the exciton can move, the higher the energy it must have. This supports the spectra moving towards the blue light wavelengths (higher energy) with the addition of oxidant.

It is generally expected that if a polymers absorbance goes down (the amount of light it “collects”) its fluorescence (the amount of collected light emitted) will also go down. It might also be expected that the introduction of defects (dopants) in the polymer chain would significantly reduce the fluorescence yield. Therefore it was very unexpected that the fluorescence measurement in the MEH-PPV oxidation experiment stayed relatively constant. This could be due to two things. First it could mean that the exciton is not being quenched by the positive charge. This is a good thing, if the exciton were quenched by the positive charge it would mean that doping could actually reduce a solar cells efficiency. Second, this could mean

that the exciton and the positive charge (polaron) do not move, i.e. they are very localized. More work needs to be done to evaluate this effect and carefully compare the absorbance and fluorescence yield.

Acknowledgements

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Figures

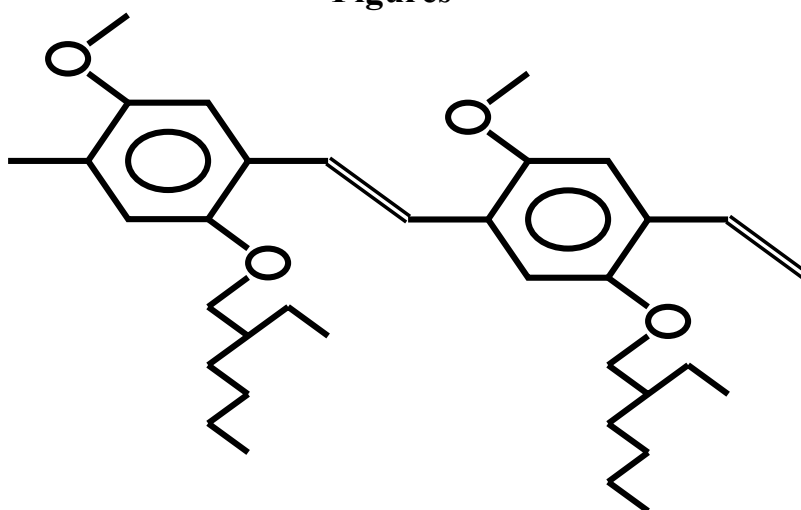


Figure 1. the structure of MEH-PPV the backbone has alternating double and single bonds to carry charge

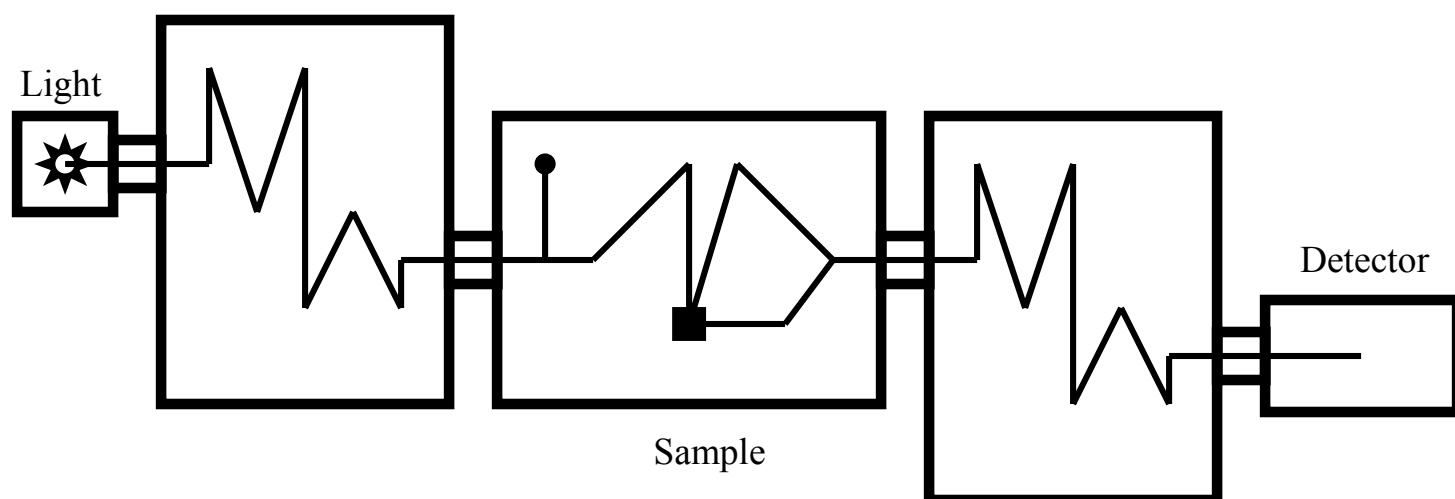


Figure 2. Fluorolog

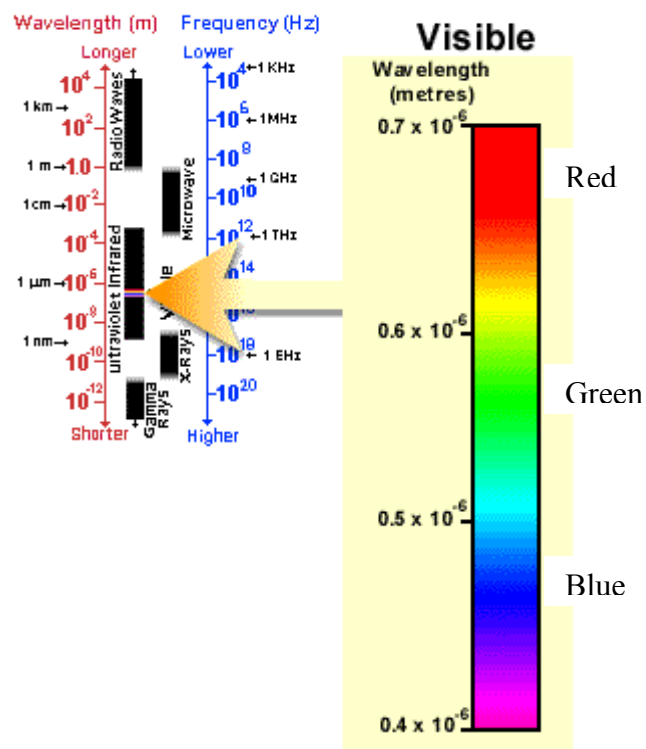


Figure 3. The visible spectrum

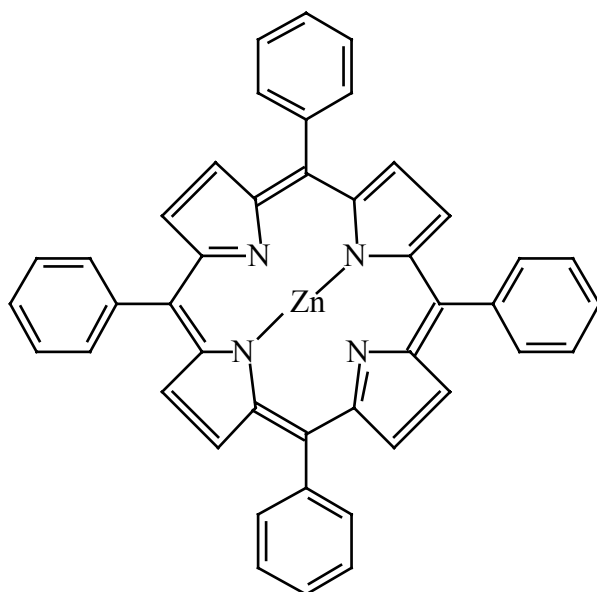


Figure 4. ZnTPP

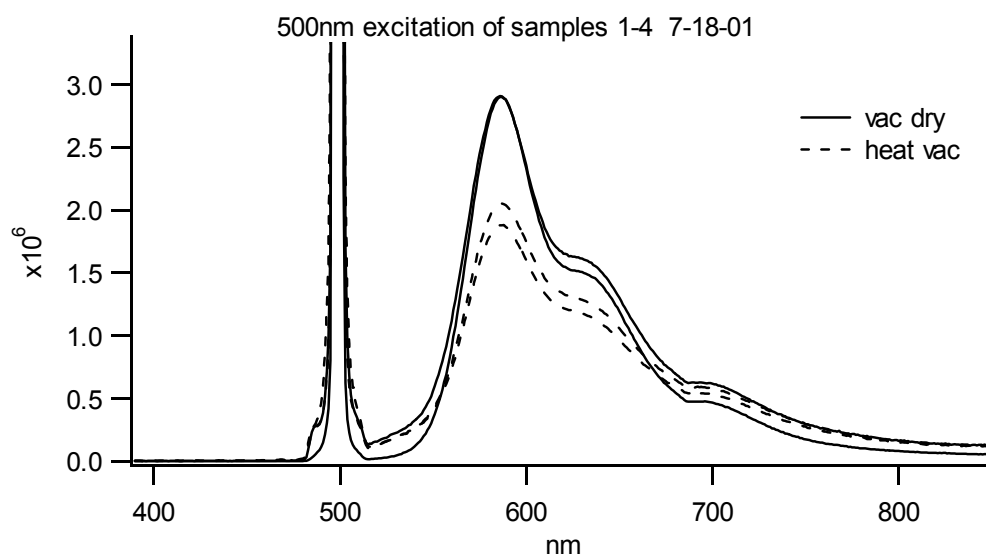


Figure 5. The fluorescence spectra of the vacuum dried and heated MEH-PPV thin films excited with 500nm light

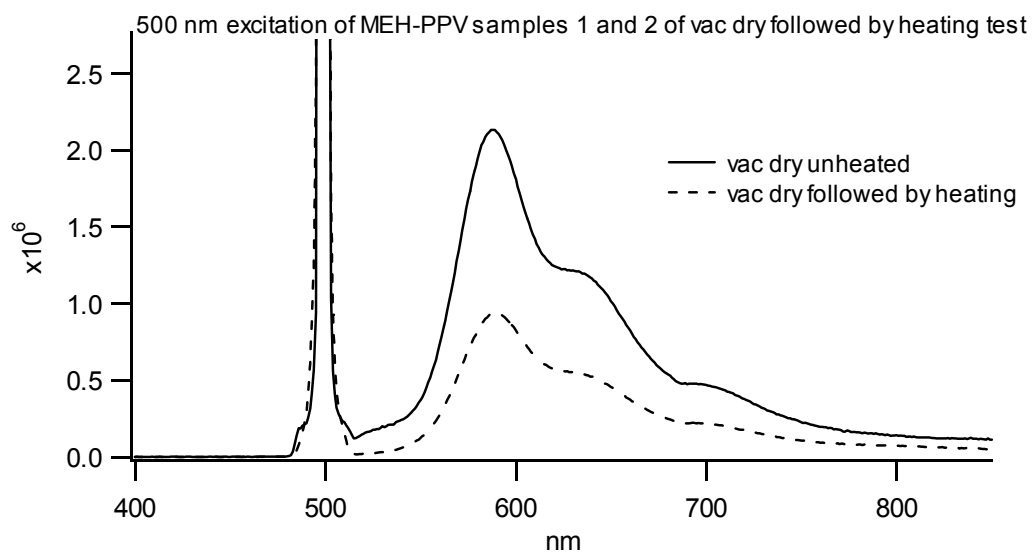


Figure 6. The fluorescence spectra of a MEH-PPV thin film dried under high vacuum and a MEH-PPV thin film that was dried under high vacuum and then subsequently heated

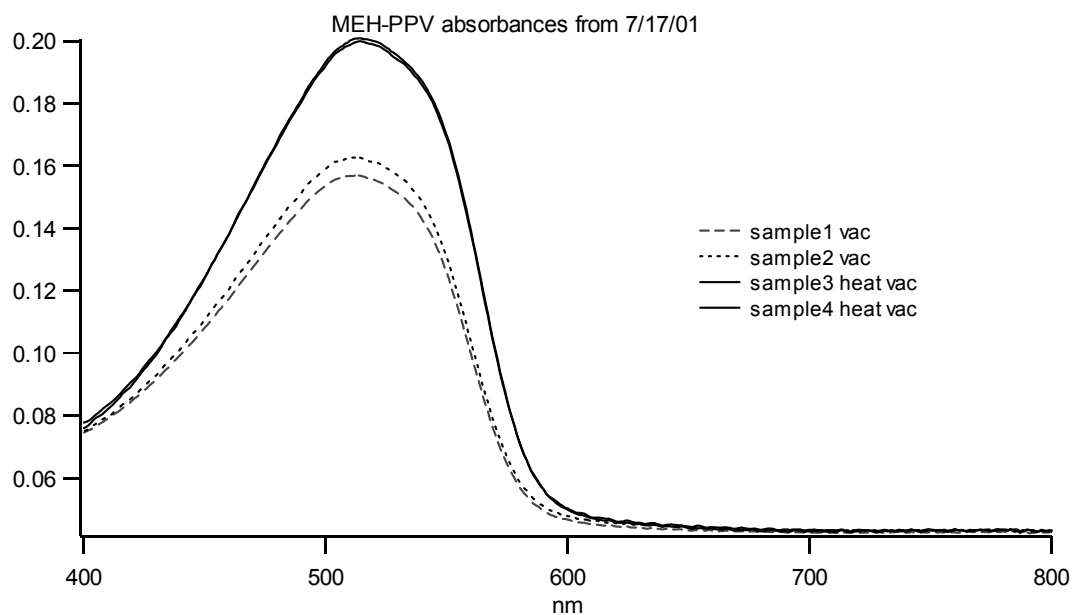


Figure 7. The absorbance spectra taken for the MEH-PPV thin films that were heat dried with a roughing vacuum and dried under high vacuum

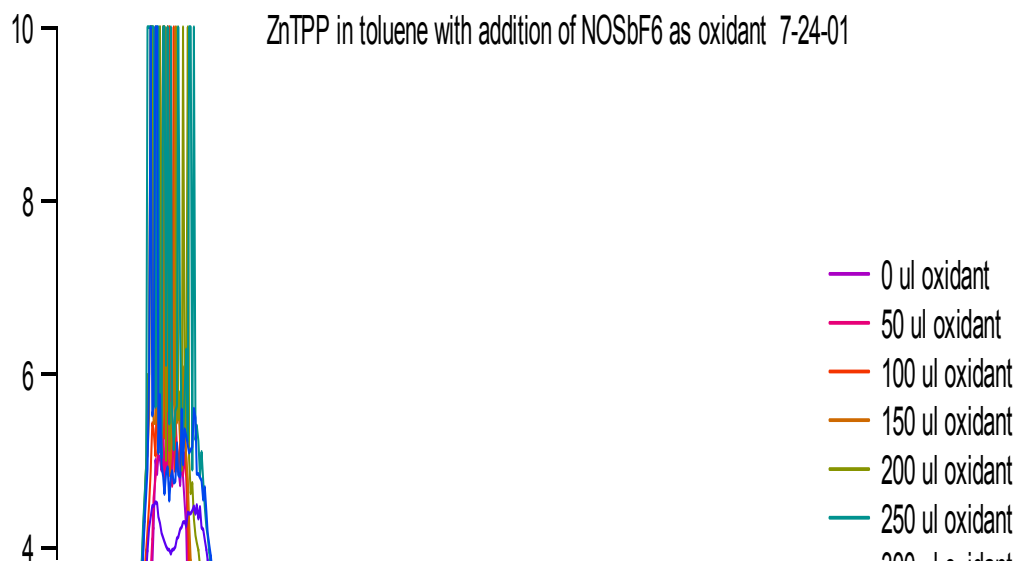


Figure 8. The absorbance spectra of the ZnTPP solution with increasing concentration of NOSbF6. The isosbestic point is at approximately 530 nm.

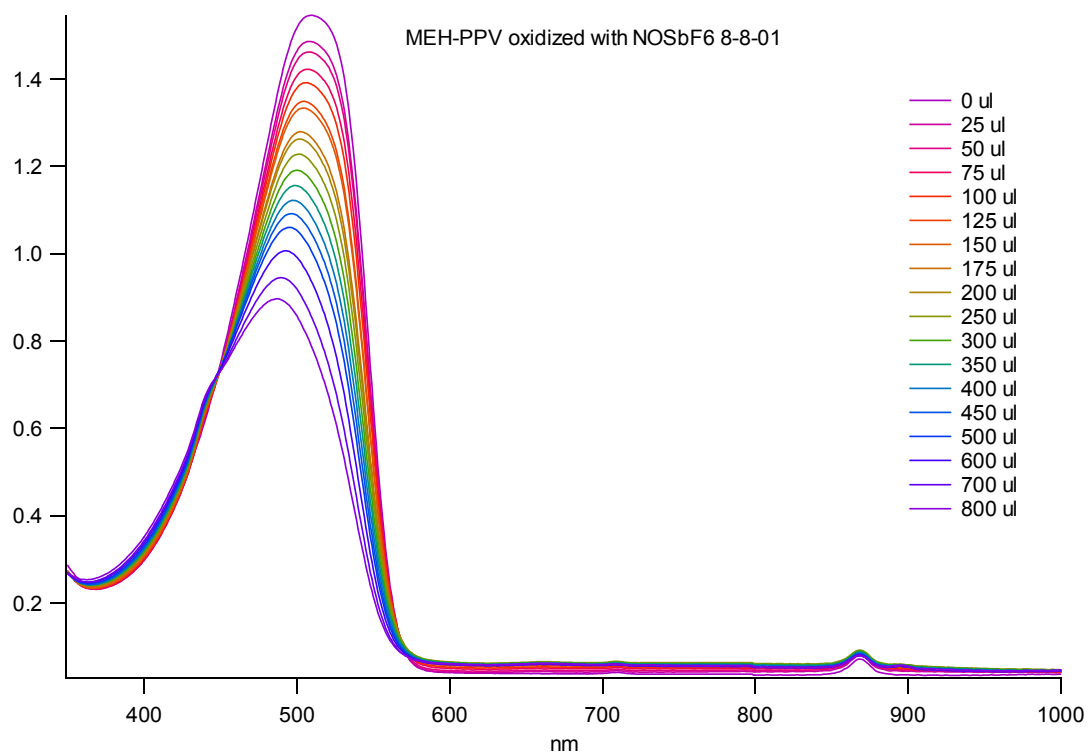


Figure 9. The absorbance spectrums showing the oxidation of MEH-PPV

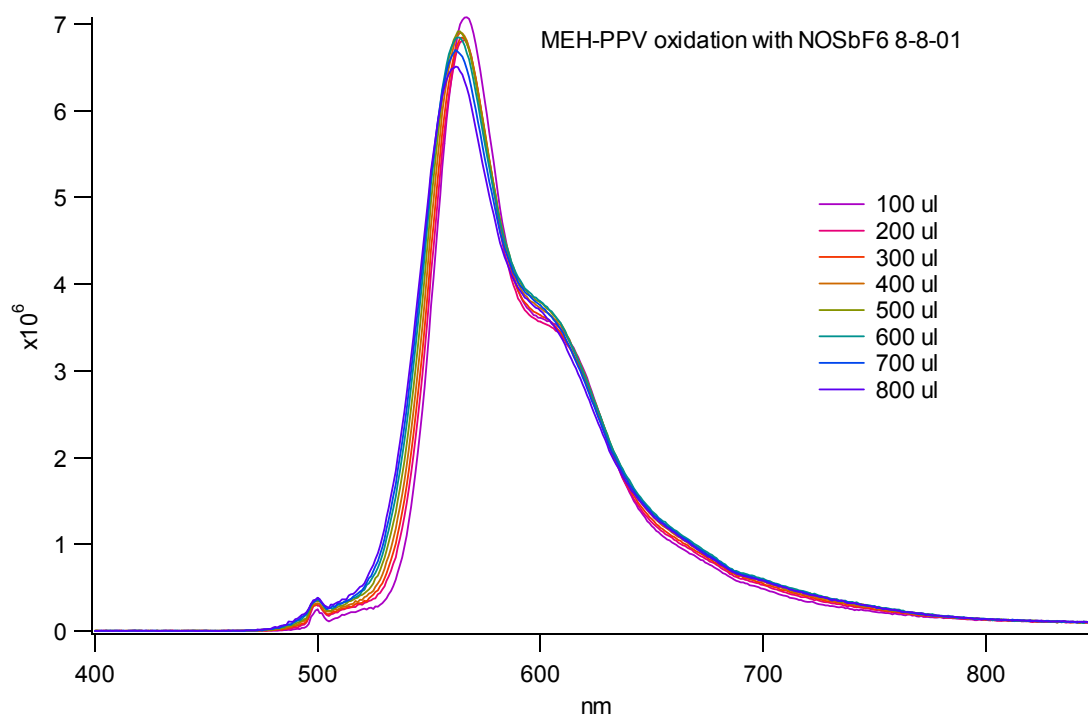


Figure 10. The fluorescence spectra showing the oxidation of MEH-PPV